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(71) Applicant: 3M INNOVATIVE PROPERTIES COMPANY [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(72) Inventors: KUBICEK, Brian, A.; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). SAVU, Patricia, M.; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). HAUSER, Edward, R.; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). PETRIN, Jason, T.; Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agents: JORDAN, Robert, H. et al.; Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

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(54) Title: LATEX PAINT COMPOSITIONS AND COATINGS

(57) Abstract: A latex paint composition comprises (a) a polymer having interpolymerized units that comprise units derived from styrene, methyl styrene, vinyl, or combinations thereof and units derived from one or more acrylates, methacrylates, acrylonitrile, or combinations thereof, (b) hiding pigment, (c) non-cellulosic thickener, and (d) at least about 0.05 weight per volume percent fluorochemical acrylic polymer additive comprising (1) at least one perfluoroalkyl moiety selected from the group consisting of heptafluoropropanesulfonamido, nonafluorobutanesulfonamido, undecafluoropentanesulfonamido, and tridecafluorohexanesulfonamido moieties and (2) at least one polyoxyalkylene block comprising at least one alkyleneoxy moiety. Also, methods for providing paint coatings with such compositions.

WO 2004/000957 A1

LATEX PAINT COMPOSITIONS AND COATINGS**FIELD**

5 The present invention relates to latex paint compositions and coatings comprising short chain fluorochemicals and to methods for imparting improved stain and soil resistance to latex paints.

10 BACKGROUND

 Latex paints are often preferred over solvent-based paints because of their improved safety, lower toxicity, and lower volatile-organic contents. Generally, however, latex paints, particularly flat latex paints, have
15 poor stain and soil resistance. Because of their highly porous nature and rough surface texture, flat latex paints tend to absorb stains. Penetrating type stains, such as ink, soft drinks, wine, and other colored liquids, have easy access to the interior of a flat paint film through numerous
20 pores and microchannels, and surface dirt, such as handprints, smudges, dust, and other particulate matter, can become entrapped in the bumpy, rough texture of the paint surface.

 In recent years, flat latex paints having improved
25 stain and soil resistance with resulting improved cleanability have been formulated (see, for example, EP 0 614 955). In addition, various additives, including hydrocarbon acrylic polymers and fluorine-containing compounds, have been used to impart improved stain and soil
30 resistance to latex paints. Consumers, however, desire flat latex paints that can provide still better stain and soil resistance with resulting improved cleanability.

SUMMARY

In view of the foregoing, we recognize that there is a need to improve the stain and soil resistance of latex paints, particularly flat latex paints, without detracting from the other desirable properties of the paint such as, for example, improved safety and minimized environmental impact.

Briefly, in one aspect, the present invention provides latex paint compositions and coatings (as used herein, the term "coating" refers to the latex paint composition after it has been applied to a substrate and has dried) that have improved stain and soil resistance with resulting improved cleanability. The compositions comprise a latex paint comprising (a) a polymer having interpolymerized units that comprise units derived from styrene, methyl styrene, vinyl, or combinations thereof and one or more units derived from acrylates, methacrylates, acrylonitrile, or combinations thereof, (b) hiding pigment, (c) non-cellulosic thickener, and (d) at least 0.05 weight per volume percent fluorochemical acrylic polymer additive comprising (1) at least one perfluoroalkyl moiety selected from the group consisting of heptafluoropropanesulfonamido, nonafluorobutanesulfonamido, undecafluoropentanesulfonamido, and tridecafluorohexanesulfonamido moieties and (2) at least one polyoxyalkylene block comprising at least one alkyleneoxy moiety; wherein said fluorochemical acrylic polymer comprises about 5 to about 30 weight percent carbon-bonded (that is, covalently bonded) fluorine based upon the total weight of said fluorochemical acrylic polymer, and said latex paint composition has a pigment volume concentration of at least 20% and less than its critical pigment volume concentration.

In other aspects, this invention also provides articles with at least one surface of the article coated with the paint compositions of the invention, and methods of imparting stain and soil resistance to a latex paint. The methods comprise (a) providing a latex paint composition comprising (1) a polymer having interpolymerized units that comprise units derived from styrene, methyl styrene, vinyl, or combinations thereof and units derived from one or more acrylates, methacrylates, acrylonitrile, or combinations thereof, (2) hiding pigment, and (3) non-cellulosic thickener; wherein said latex paint has a pigment volume concentration of at least 20% and less than its critical pigment volume concentration; (b) adding at least about 0.05 weight per volume percent of a fluorochemical acrylic polymer additive comprising (1) at least one perfluoroalkyl moiety selected from the group consisting of heptafluoropropanesulfonamido, nonafluorobutanesulfonamido, undecafluoropentanesulfonamido, and tridecafluorohexanesulfonamido moieties and (2) at least one polyoxyalkylene block comprising at least one alkyleneoxy moiety; wherein said fluorochemical acrylic polymer has about 5 to about 30 weight percent carbon-bonded fluorine based upon the total weight of said fluorochemical acrylic polymer to said latex paint composition; (c) applying the resulting composition of (b) to a substrate surface; and (d) allowing said resulting composition to dry such that a coating with a fluorine-enriched surface is formed on said substrate surface. As used herein, a "fluorine-enriched surface" refers to the surface of a coating that contains more fluorine at the surface than in the bulk.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

It has been discovered that the fluorochemical acrylic polymer additives described herein, particularly those derived from perfluorobutanesulfonyl fluoride (PBSF),
5 impart improved stain and soil resistance and repellency into the latex paint composition of the invention. Surprisingly, these fluorochemical acrylic polymers impart comparable, and in some instances better, stain and soil resistance and repellency than fluorochemical acrylic
10 polymers with longer perfluoroalkyl segments such as perfluorooctanesulfonyl fluoride (POSF).

In light of the prior art, one would expect that coatings derived from shorter fluorochemical chains would not be as effective at imparting stain and soil resistance
15 and repellency as those derived from longer fluorochemical chains. For instance, in the art of surfactants, particularly surfactants with fluorochemical chains, there is a preference for those with longer fluorochemical chains (for example, C₆ - C₁₀ in U.S. Patent No. 2,803,615
20 (Ahlbrecht et al.) and C₆ - C₁₂ in U.S. Patent No. 3,787,351 (Olson)). It has been observed in hydrocarbon surfactants and in surfactants derived from perfluorocarboxylic acids and sulfonic acids that increasing the chain length of the hydrocarbon chains decreases the critical micelle
25 concentration (that is, less surfactant is needed in order to obtain the desired surface modification)(see, for example, AMPHOTERIC SURFACTANTS, edited by Eric G. Lomax, Marcel Dekker Inc. (1996); ORGANOFLUORINE CHEMICALS AND THEIR INDUSTRIAL APPLICATIONS, edited by R.E. Banks, Ellis
30 Horwood Ltd., p. 56 (1979); J.O. Hendricks, Ind. Eng. Chem. 45, 103 (1953); M.K. Bernett and W.A. Zisman, J. Phys. Chem. 63, 1912 (1959)).

Repellency results, in part, from low surface energies. The prior art suggests that only after the seven outermost carbon atoms of a perfluorinated carboxylic acid are fully fluorinated do the surface energies of various liquids on the surface approach those of a perfluoro fatty acid monolayer, which has a surface energy amongst the lowest ever recorded (see, for example, N.O. Brace, J. Org. Chem. 27, 4491 (1962), and W.A. Zisman, Advan. Chem., 22 (1964)). One would therefore expect the same to be true of fluorochemical acrylic polymers derived from PBSF. That is, one would expect that the surface energy of the polymer would be closely tied to the chain length of the fluorinated monomer. Yet, the fluorochemical acrylic polymers of the invention impart comparable, and in some instances better, stain and soil resistance and repellency than fluorochemical acrylic polymers with longer perfluoroalkyl segments.

It is particularly advantageous to use short chain perfluoroalkanesulfonyl fluorides, such as PBSF, to make the starting intermediates for the paint additives rather than using POSF because they can be produced at a lower cost per weight because of their higher yields (for example, by electrofluorination, the yield of PBSF is approximately 58% and the yield of POSF is approximately 31% (PREPARATION, PROPERTIES, AND INDUSTRIAL APPLICATIONS OF ORGANOFLUORINE COMPOUNDS, edited by R.E. Banks, Ellis Horwood Ltd., P. 37 (1982)) and still maintain their potency as repellants at the same weight percent.

Furthermore, it has been reported that certain pefluorooctyl-containing compounds may bioaccumulate in living organisms (see, for example, U.S. Patent No. 5,688,884 (Baker et al.)). Short chain sulfonic acids, however, are less toxic and less bioaccumulative than the longer chain homologs. For example, PBSF, tested in the

form of its potassium salt, eliminates from the body much more efficiently than POSF and perfluorohexanesulfonate (see, for example, WO 01/30873). Thus, the compositions of the invention meet the need in the art for latex paints having improved stain and soil resistance while maintaining the other desirable properties of the paint.

Paint Composition

Binding Polymer

Polymers useful as component (a), the "binding polymer", of the latex paints of the invention are copolymerization products of a mixture of co-monomers which comprise monomers selected from styrene, methyl styrene, vinyl, or combinations thereof. Preferably co-monomers comprise (more preferably consist essentially of) at least 40 mole percent of monomers selected from styrene, methyl styrene, or combinations thereof and at least 10 mole percent of one or more monomers selected from acrylates, methacrylates, and acrylonitrile. Preferably, the acrylates and methacrylates contain from 4 to 16 carbon atoms such as, for example, 2-ethylhexyl acrylate and methyl methacrylates. It is also preferable that the monomers be used in a proportion such that the final polymer has a glass-transition temperature (T_g) greater than 21°C and less than 95°C. The polymers preferably have a weight-average molecular weight of at least 100,000.

Preferably, the binding polymer comprises interpolymerized units derived from 2-ethylhexyl acrylate. More preferably, the binding polymer comprises polymerized units comprising from 50 to 70 mole percent of units derived from styrene, methyl styrene, or combinations thereof; from 10 to 30 mole percent of units derived from 2-ethylhexyl acrylate; and from 10 to 30 mole percent of units derived

from methyl acrylate, acrylonitrile, or combinations thereof.

Illustrative examples of suitable binding polymers include a copolymer whose interpolymerized units are derived from about 49 mole percent styrene, 11 mole percent α -methylstyrene, 22 mole percent 2-ethylhexyl acrylate, and 18 mole percent methyl methacrylates with a Tg of approximately 45°C (available as Neocryl™ XA-6037 polymer emulsion from ICI Americas, Inc., Bridgewater, NJ); a copolymer whose interpolymerized units are derived from about 51 mole percent styrene, 12 mole percent α -methylstyrene, 17 mole percent 2-ethylhexyl acrylate, and 19 mole percent methyl methacrylates with a Tg of approximately 44°C (available as Joncryl™ 537 polymer emulsion from S.C. Johnson & Sons, Racine, WI); and a terpolymer whose interpolymerized units are derived from about 54 mole percent styrene, 23 mole percent 2-ethylhexyl acrylate, and 23 mole percent acrylonitrile with a Tg of approximately 44°C (available from B.F. Goodrich Co. as Carboset™ XPD-1468 polymer emulsion). Preferably, the binding polymer is Joncryl™ 537.

Hiding Pigment

The latex paint of the invention comprises a hiding pigment to give the paints better "hiding power" or coverage. Preferably, the hiding pigment has a refractive index above about 1.8.

Suitable hiding pigments include white opacifying hiding pigments and colored organic and inorganic pigments. Representative examples of suitable white opacifying hiding pigments include rutile and anatase titanium dioxides, lithopone, zinc sulfide, lead titanate, antimony oxide, zirconium oxide, barium sulfide, white lead, zinc oxide, leaded zinc oxide, and the like, and mixtures thereof. A

preferred white organic hiding pigment is rutile titanium dioxide. More preferred is rutile titanium dioxide having an average particle size between about 0.2 to 0.4 microns. Examples of colored organic pigments are phthalo blue and
5 hansa yellow. Examples of colored inorganic pigments are red iron oxide, brown oxide, ochres, and umbers.

Thickener

Most known latex paints contain thickeners to modify the rheological properties of the paint to ensure
10 good spreading, handling, and application characteristics. The latex paint of the invention comprises a non-cellulosic thickener (preferably, an associative thickener; more preferably, a urethane associative thickener).

Associative thickeners such as, for example,
15 hydrophobically modified alkali swellable acrylic copolymers and hydrophobically modified urethane copolymers generally impart more Newtonian rheology to emulsion paints compared to conventional thickeners such as, for example, cellulosic thickeners. Representative examples of suitable associative
20 thickeners include polyacrylic acids (available, for example, from Rohm & Haas Co., Philadelphia, PA, as Acrysol™ RM-825 and QR-708 Rheology Modifier) and activated attapulgite (available from Engelhard, Iselin, NJ as Attagel™ 40).

25 Fluorochemical Additive

The latex paint of the invention comprises at least about 0.05 weight per volume percent of a fluorochemical acrylic polymer additive ("fluorochemical additive"), which imparts improved stain and soil resistance
30 to the latex paint composition of the invention. The fluorochemical additive comprises (1) at least one perfluoroalkyl moiety chosen from the group consisting of

heptafluoropropanesulfonamido, nonafluorobutanesulfonamido, undecafluoropentanesulfonamido, and tridecafluorohexanesulfonamido moieties and (2) at least one polyoxyalkylene block comprising at least one alkyleneoxy moiety.

The perfluoroalkyl moieties useful in the invention are generally soluble over a wide range of polarity. Preferably, the perfluoroalkyl moiety is heptafluoropropanesulfonamido or nonafluorobutanesulfonamido. More preferably, the perfluoroalkyl moiety is nonafluorobutanesulfonamido.

Preferably, a plurality of perfluoroalkyl moieties is each linked to at least one polyoxyalkylene block by a polymer chain. The polyoxyalkylene blocks comprise at least one alkyleneoxy moiety. The alkyleneoxy moiety generally has 2 to 6 carbon atoms (preferably, 2 to 4 carbons atoms; more preferably, 2 or 3 carbon atoms). Preferred alkyleneoxy moieties include, for example, ethyleneoxy moieties and propyleneoxy moieties. Propyleneoxy moieties can be branched or linear.

When ethyleneoxy moieties and propyleneoxy moieties are linked together, they form polyoxyethylene and polyoxypropylene blocks respectively. Preferably, at least one polyoxypropylene block is attached to a polyoxyethylene block. Additional blocks of polyoxyethylene or polyoxypropylene can be present in random order as well. Such materials having an average molecular weight of about 500 to about 15,000 are commonly available under trade names such as, for example, Pluronic™ (or Pluronic™ R, a reverse Pluronic structure) from BASF Corporation.

More preferably, the polyoxypropylene block is also attached to a second polyoxyethylene block (or the polyoxyethylene block is attached to a second

polyoxypropylene block). Particularly useful block polymers include those, for example, comprising a center block having from about 20 to about 55 propyleneoxy moieties and blocks to each side of the center block each having from about 5 to about 130 ethyleneoxy moieties. Other particularly useful block polymers include those comprising a center block having from about 15 to 165 ethyleneoxy moieties and blocks to each side of the center block each having from about 5 to about 25 propyleneoxy moieties.

Other preferred alkyleneoxy moieties are those derived from polyethylene glycols having a molecular weight of about 200 to about 10,000. Commercially available polyethylene glycols that are suitable for use in the invention include, for example, Carbowax™ (available from Union Carbide).

The acrylate portion of the fluorochemical additive comprises acrylate and/or methacrylate moieties. Acrylate and/or methacrylate moieties form part of the starting monomers as well as the final polyacrylate products. For example, nonafluorobutanesulfonamido acrylate can be copolymerized with a polyalkyleneoxy moiety to form surface-active agents. Thus, the fluorochemical acrylic polymer additives useful in the paint composition of the invention can be prepared, for example, by free radical initiated copolymerization of a nonafluorobutanesulfonamido radical-containing acrylate with a polyalkyleneoxy acrylate such as, for example, monoacrylate, diacrylate or mixtures thereof. The molecular weight of the polyacrylate copolymer can be controlled by adjusting the concentration and activity of initiator, concentration of monomers, and temperature, or by chain-transfer agents. The preparation of such polyacrylates and starting nonafluorobutanesulfonamido acrylates are known in the art

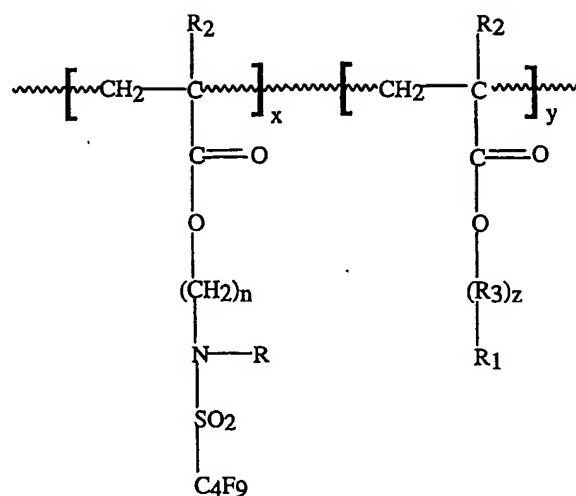
(see, for example, U.S. Patent Nos. 3,787,351 (Olson) and 2,803,615 (Ahlbrecht et al.).

The polyalkyleneoxy acrylates can be prepared from commercially available hydroxypolyethers or polyoxyalkylene hydroxy compounds such as, for example, Pluronic™ or Carbowax™ polymers. Such hydroxy materials are reacted with acrylic acid, acrylyl chloride, or acrylic anhydride using methods known in the art. Alternatively, a polyalkyleneoxy diacrylate can be copolymerized with the nonafluorobutanesulfonamido acrylate to obtain a polyacrylate copolymer of the invention.

The above-described fluorochemical additives can optionally comprise a water-solubilizing polar group, which can be anionic, nonionic, cationic, or amphoteric. Preferably, the water-solubilizing polar group is anionic. More preferably, it is selected from the group consisting of sulfonates, sulfates, and carboxylates (for example, $-\text{SO}_3\text{M}$, $-\text{OSO}_3\text{M}$, and $-\text{C}(=\text{O})\text{OM}$ wherein M is hydrogen, a metal cation such as an alkali or alkaline earth metal cation (for example, sodium, potassium, calcium, or magnesium, and the like), or a nitrogen-based cation such as, for example, ammonium or a protonated tertiary amine (for example, $(\text{HOCH}_2\text{CH}_2)_2\text{N}^+\text{HCH}_3$)).

The fluorochemical additives useful in the paint composition of the invention include those that can be represented by the following general formula:

Formula 1



wherein \sim represents a bond in a polymerizable or polymer chain; R, R₁ and R₂ are each independently hydrogen or alkyl of 1 to 4 carbon atoms; R₃ is at least one or more straight or branched alkyleneoxy groups, linked together and having 2 to 6 carbon atoms, or a straight or branched alkylene group having 12 to 20 carbon atoms; n is an integer from 2 to 10; and x, y and z are integers of at least 1.

Preferred fluorochemical additives of Formula I include those in which R, R₁ and R₂ are each independently hydrogen or methyl and those in which n is 2.

Another preferred embodiment is that in which R₃ is a polyalkylene oxide group selected from those represented by formula A or formula B:

Formula A



Formula B



wherein EO is an ethyleneoxy moiety, PO is a propyleneoxy moiety, p is an integer of 1 to about 165, and q is an integer of 0 to about 55.

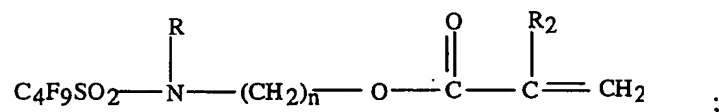
Preferably, when R₃ is a polyalkylene oxide group of Formula A, p is an integer of about 5 to about 130 and q is an integer of about 20 to about 55. More preferably, p

is about 11 and q is about 21. Even more preferably, p is about 11, q is about 21, and R is methyl.

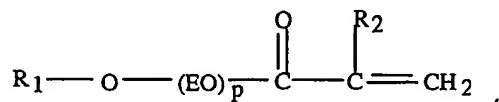
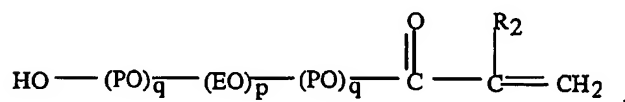
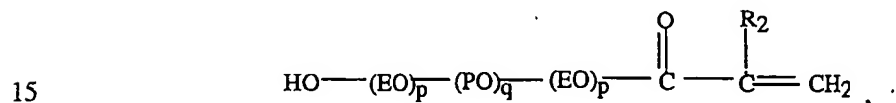
Preferably, when R₃ is a polyalkylene oxide group of Formula B, q is an integer of about 5 to about 25 and p is an integer of about 10 to about 165.

The fluorochemical additives useful in the paint composition of the invention also include the reaction products of the following monomers or oligomers:

(i) a compound represented by the following general formula:

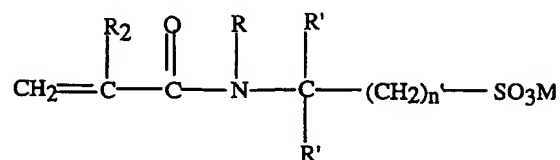


(ii) a compound selected from the group consisting of



and mixtures thereof; and

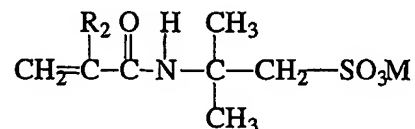
(iii) a compound represented by the following general formula:



wherein R, R₁, R₂, R' are hydrogen or alkyl of 1 to 4 carbon atoms, EO is an ethyleneoxy moiety, PO is a propyleneoxy

moiety, p is an integer of 1 to about 130, q is an integer of 0 to about 55, n is an integer of 2 to about 10, n' is an integer of 1 to about 10, and M is hydrogen, a cation, or a protonated tertiary amine.

- 5 Preferably, (iii) is a compound represented by the following general formula:



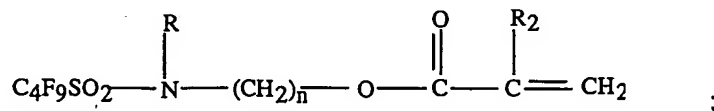
- wherein R₂ is hydrogen or methyl and M is hydrogen, potassium, ammonium, lithium, or a protonated tertiary amine.
- 10

In a particularly useful embodiment, the fluorochemical additive comprises the reaction product of (i), (ii), (iii), and (iv) wherein (iv) is a compound represented by the general formula A-O-C(=O)C(R₂)=CH₂; where A is an amine-containing group or an alkyl of 12 to 20 carbon atoms.

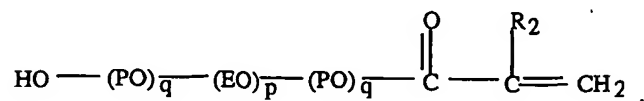
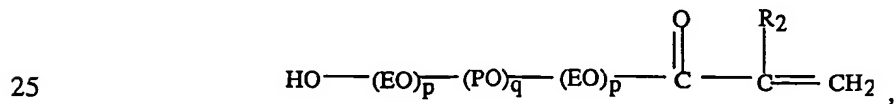
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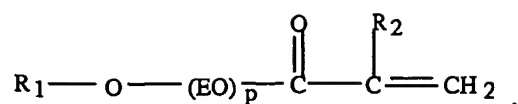
The fluorochemical additives useful in the paint composition of the invention also include the reaction products of the following:

- 20 (i) a compound represented by the following general formula:



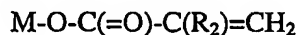
- (ii) a compound selected from the group consisting of





and mixtures thereof; and

(iii) a compound represented by the following
 5 general formula:



Wherein R, R₁, R₂, and R' are independently hydrogen or alkyl
 of 1 to 4 carbons atoms, n is an integer of 2 to about 10,
 EO is an ethyleneoxy moiety, PO is a propyleneoxy moiety, p
 10 is an integer of 1 to about 130, q is an integer of 0 to
 about 55, and M is H, potassium, sodium, ammonium, or
 protonated tertiary amine. Preferably, M is H or ammonium.

In a particularly useful embodiment, the
 fluorochemical additive comprises the reaction product of
 15 (i), (ii), (iii), and (iv) wherein (iv) is a compound
 represented by the general formula A-O-C(=O)C(R₂)=CH₂; where
 A is an amine-containing group or an alkyl of 12 to 20
 carbon atoms.

In pure form, the fluorochemical additives useful
 20 in the paint compositions of the invention are typically
 viscous liquids or glassy solids. They are soluble in polar
 synthetic resinous compositions and have about 5 to about 30
 weight percent carbon-bonded fluorine based upon the total
 weight of the fluorochemical additive (preferably, about 10
 25 to about 25 weight percent).

The latex paint composition of the invention
 comprises at least about 0.05 weight per volume percent
 fluorochemical additive (preferably at least about 0.1
 weight per volume percent). The amount of fluorochemical
 30 additive generally ranges up to about 3 weight per volume
 percent (preferably up to about 0.3 weight per volume

percent). More fluorochemical additive can be used (up to about 10 weight per volume percent), but the use of high concentrations will typically, at some point, become cost prohibitive.

5 Other Ingredients

Latex-paint films are formed by coalescence of the binding polymer to form a binding matrix at the ambient paint application temperature to form a hard, tack-free film. Coalescing solvents aid the coalescence of the film-forming binder by lowering the film-forming temperature. The latex paints of the invention preferably contain a coalescing solvent. Representative examples of suitable coalescing solvents include 2-phenoxyethanol, diethylene glycol butyl ether, dibutyl phthalate, diethylene glycol, 2,2,4-trimethyl-1,1,3-pentanediol monoisobutyrate, and combinations thereof. Preferably, the coalescing solvent is diethylene glycol butyl ether (butyl carbitol) (available from Sigma-Aldrich, Milwaukee, WI) or 2,2,4-trimethyl-1,1,3-pentanediol monoisobutyrate (available from Eastman Chemical Co., Kingsport, TN, as Texanol™), or combinations thereof.

Coalescing solvent is preferably utilized at a level between about 12 to 60 grams (preferably about 40 grams) of coalescing solvent per liter of latex paint or at about 20 to 30 weight percent based on the weight of the polymer solids in the paint.

Paints can be manufactured to have a desired degree of gloss or shininess. Paint gloss is defined using ASTM Test Method D523 "Standard Test Method for Specular Gloss." Gloss ratings by this test method are obtained by comparing the reflectance from the specimen (at an angle of 20°, 60°, or 85° measured from the vertical) to that from a polished glass standard. Gloss readings at 20° describe the "depth" of gloss and are typically only used to describe

gloss or semi-gloss paints. Gloss readings at 60° are used to describe most paints, except for completely flat paints. Gloss readings at 85° describe the "sheen" of flat, eggshell, and satin paints.

- 5 Typically, paints are categorized by their gloss values. For example, the Master Paint Institute (MPI) categorizes paints as follows:

<u>Type of Paint</u>	<u>20° Gloss</u>	<u>60° Gloss</u>	<u>85° Gloss</u>
Gloss	20 - 90	70 - 85+	--
Semi-gloss	5 - 45	35 - 75	--
Satin	--	20 - 35	min. 35
Eggshell	--	10 - 25	10 - 35
Flat/matte	--	0 - 10	max. 35

- The latex paints of the invention preferably have an 85° gloss less than or equal to about 20 and would therefore typically be considered eggshell or flat paints.

- Flatter paints can be produced using various approaches. One approach is to increase the pigment volume concentration (that is, the ratio by volume of all pigments in the paint to total nonvolatiles) (PVC) of the paint above its critical pigment volume concentration (CPVC). At the CPVC, many physical and optical properties of paint change abruptly and the paint changes from a semi-gloss paint to a flat paint. Typically, though, high PVC flat paints exhibit less durability than lower PVC flat paints, all else being equal, because these flat paints have less binder available per unit of pigment.

- Alternatively, a flat paint can be produced by adding a flattening agent (that is, a material which reduces the gloss of a paint film). Flattening agents introduce micro-roughness to the surface causing the light to be reflected in a diffuse manner, which reduces the apparent

gloss. This latter approach generally produces a better paint film.

Therefore, the flat paints of the present invention have a PVC of at least 20% and less than their CPVC, but preferably contain a flatting agent. Preferably, the PVC is below about 54%; more preferably, below about 52%. Suitable flatting agents include silicas of various types such as, for example, Novacite™ Silica (available from Malvern Minerals, Hot Springs National Park, AR).

The paints of this invention may further comprise conventional materials used in paints such as, for example, plasticizer, anti-foam agent, pigment extender, pH adjuster, tinting color, and biocide. Such typical ingredients are listed, for example, in TECHNOLOGY OF PAINTS, VARNISHES AND LACQUERS, edited by C.R. Martens, R.E. Kreiger Publishing Co., p. 515 (1974).

Paints are commonly formulated with "functional extenders" to increase coverage, reduce cost, achieve durability, alter appearance, control rheology, and influence other desirable properties. Examples of functional extenders include, for example, barium sulphate, calcium carbonate, clay, gypsum, silica, and talc.

The most common functional extenders for interior flat paints are clays. Clays have a number of properties that make them desirable. Inexpensive calcined clays, for example, are useful in controlling low-shear viscosity and have a large internal surface area, which contributes to "dry hide". But, this surface area is also available to trap stains.

Because of their tendency to absorb stains, it is preferable that calcined clays are used in the paints of the invention only in the small amounts required for rheology control, for example, typically as less than about half of

the total extender pigment, or are not used at all. The preferred extenders for use in the paints of the invention are calcium carbonates; most preferred are ultra-fine ground calcium carbonates such as, for example, Opacimite™

5 (available from ECC International, Sylacauga, AL), Supermite™ (available from Imerys, Roswell, GA), or others having particle size of approximately 1.0 to 1.2 microns. Ultra-fine calcium carbonate help to space titanium dioxide optimally for hide (see, for example, K.A. Haagenson, "The
10 effect of extender particle size on the hiding properties of an interior latex flat paint," American Paint & Coatings Journal, April 4, 1988, pp. 89 - 94).

Preparation of the Paint Composition

The latex paints of the invention can be prepared
15 utilizing conventional techniques. For example, some of the paint ingredients are generally blended together under high shear to form a mixture commonly referred to as "the grind" by paint formulators. The consistency of this mixture is comparable to that of mud, which is desirable in order to
20 efficiently disperse the ingredients with a high shear stirrer. During the preparation of the grind, high shear energy is used to break apart agglomerated pigment particles.

The ingredients not included in the grind are
25 commonly referred to as "the letdown." The letdown is usually much less viscous than the grind, and is usually used to dilute the grind to obtain a final paint with the proper consistency. The final mixing of the grind with the letdown is typically carried out with low shear mixing.

30 Most polymer latexes are not shear stable, and therefore are not used as a component of the grind. Incorporation of shear unstable latexes in the grind can

result in coagulation of the latex, yielding a lumpy paint with no, or little, film-forming capability. Consequently, paints are generally prepared by adding the latex polymer in the letdown.

5 However, the preferred paints of this invention contain latex polymers that are generally shear stable. Therefore, the latex paints of the invention can be prepared by incorporating some or all of the latex polymer into the grind. Preferably, at least some of the latex polymer is
10 put in the grind.

Method of Imparting Stain and Soil Resistance

 The fluorochemical acrylic polymer additives described above can be used to impart improved stain and soil resistance to latex paint compositions that have a
15 pigment volume concentration of at least 20% and less than its critical pigment volume concentration and that comprise (a) a polymer having interpolymerized units that comprise units derived from styrene, methyl styrene, vinyl, or combinations thereof and units derived from one or more
20 acrylates, methacrylates, acrylonitrile, or combinations thereof, (b) hiding pigment, and (c) noncellulosic thickener. Preferably, the polymer's interpolymerized units comprise at least 10 mole percent of units derived from styrene, methyl styrene, or combinations thereof and at
25 least 10 mole percent of units derived from one or more acrylates, methacrylates, acrylonitrile, or combinations thereof. A latex paint coating with improved stain and soil resistance can be obtained by providing such a latex paint composition, adding at least 0.05 weight per volume percent
30 fluorochemical acrylic polymer additive, applying the resulting composition to a substrate surface, and allowing the resulting composition to dry such that a coating with a

fluorine-enriched surface is formed on the substrate surface.

The fluorochemical additive can be added to the latex paint composition at any point during or after its formulation (for example, during the grind or the letdown or after all other ingredients have been blended). Preferably, the fluorochemical additive is added during the letdown.

The resulting latex paint composition can be applied to various substrate surfaces, such as, for example architectural surfaces such as walls and ceilings, articles such as furniture and boxes, or any other surface that is normally painted.

The resulting composition should be allowed to dry in a manner that allows the fluorochemical additive to migrate to the surface of the coating as it dries so that the resulting dried coating has a fluorine-enriched surface. Preferably, the composition is allowed to dry on the substrate surface under typical indoor temperature (about 10°C (50°F) to about 40°C (100°F)) and humidity (about 20% to about 90% relative humidity) conditions.

EXAMPLES

The invention will be further explained by the following illustrative examples which are intended to be non-limiting.

Glossary Table

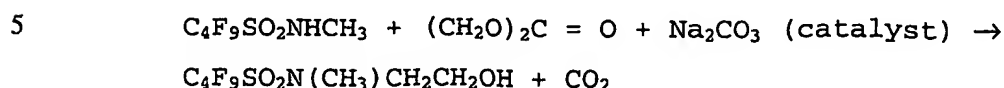
Descriptor	Description, Structure and/or Formula	Availability/ Preparation
AA	Acrylic acid	Sigma-Aldrich, Milwaukee, WI
Acrysol	ACRYSOL TM RM-825; Thickener	Rohm and Haas Co., Philadelphia, PA

AMPS	2-Acrylamido-2-methyl-1-propanesulfonic acid; $\text{H}_2\text{C}=\text{CHC}(\text{O})\text{NHC}(\text{CH}_3)_2\text{CH}_2\text{SO}_3\text{H}$	Sigma-Aldrich, Milwaukee, WI
Attagel	ATTAGEL TM 40; activated attapulgate	Engelhard, Iselin, NJ
Butyl Carbitol	diethylene glycol butyl ether	Sigma-Aldrich, Milwaukee, WI
Colortrend	Raw UMBER 888-2009; Premixed with water (1:10)	Degussa, Philadelphia, PA
CW750A	$\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_{17}\text{C}(\text{O})\text{CH}=\text{CH}_2$	US Pat. No. 3,728,151 (Sherman, et al., Example 17)
DMAEMA	Dimethylaminoethyl methacrylate	Sigma-Aldrich, Milwaukee, WI
Drew	DREWPLUS TM L- 475	Ashland Specialty Chemical Co, Dublin, OH
Joncryn	JONCRYL TM 537	Johnson Polymer, Inc, Sturtevant, WI
Kaolin	KAOPATE TM Clay	Thiele Kaolin Co., Sandersville, GA
MeFBSEA	$\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{CH}=\text{C}$ H_2	See Preparation 1 below
MeFBSEMA	$\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$	See Preparation 2 below
Novacite	NOVACITE TM 1250; Silica	Malvern Minerals, Hot Springs National Park, AR
Nuosept	NUOSEPT TM 95; Biocide	Degussa, Philadelphia, PA
Pluronic	PLURONIC TM Acrylate $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{11}[\text{CH}(\text{CH}_3)\text{CH}_2\text{O}]_{21}(\text{C}$ $\text{H}_2\text{CH}_2\text{O})_{11}\text{C}(\text{O})\text{CH}=\text{CH}_2$	US Pat. No. 3,787,351 (Olson, Example 1)
Propylene Glycol	$\text{CH}_3\text{CHOHCH}_2\text{OH}$	Sigma-Aldrich, Milwaukee, WI
Stearyl methacrylate	$\text{C}_{18}\text{H}_{37}\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$	Sigma-Aldrich, Milwaukee, WI
Supermite	SUPERMITE TM ; CaCO_3	Imerys, Roswell, GA
Texanol	TEXANOL TM ester alcohol	Eastman Chemical Company, Kingsport, TN
Ti-Pure	TI-PURE TM titanium dioxide; R900	DuPont, Wilmington, DE
Zonyl	ZONYL TM 8867-L; Fluorochemical Urethane	DuPont, Wilmington, DE

Preparation 1: Synthesis of MeFBSEA

Ethoxylation of MeFBSA with Ethylene Carbonate

REACTION:



CHARGES:

- 5 A. 100 g MeFBSA ($C_4F_9SO_2NHCH_3$, MW = 313, 0.32 moles)
 B. 2.8 g Na_2CO_3 (0.026 moles)
 D1. 8 g ethylene carbonate (MW = 88) (available from
 Sigma-Aldrich, Milwaukee, WI) melted in oven at
 50°C
 D2. 8 g ethylene carbonate
 D3. 8 g ethylene carbonate
10 D4. 10 g ethylene carbonate (total weight = 34 g, 0.38
 moles)
 E. 300 ml water
 F. 300 ml water
 G. 300 ml 3 wt% sulfuric acid
 H. 300 ml water
15 I. 300 ml water
 J. 300 ml water

PROCEDURE:

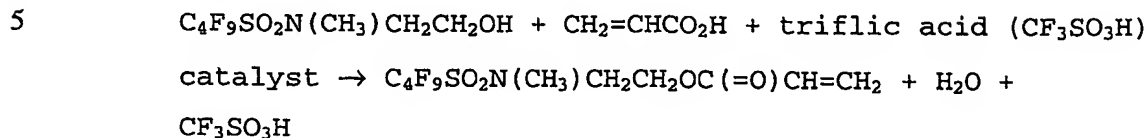
1. Charges A, B, and C were placed in a one liter 3-necked
 flask with an overhead stirrer, thermocouple, addition
20 funnel, and reflux condenser.
2. The batch was heated to 60°C (140°F) at which point the
 batch was molten and the stirring was begun. The set
 point was increased to 120°C (248°F).
3. When the batch reached 120°C, Charge D1 was removed
25 from the oven and transferred to the addition funnel.
 Charge D1 was then added slowly over a period of 10
 minutes. Outgasing (carbon dioxide) was observed.
 Thirty minutes elapsed until the rate of outgasing was
 noticed to have diminished.
30 4. Charge D2 was then transferred to the addition funnel
 and added over a period of 5 minutes. After 25
 minutes, the rate of outgasing had slowed and Charge D3
 was added over a 5 minute period. After 30 minutes,

Charge D4 was removed from the oven, added to the addition funnel and added to the batch over a 5 minute period.

- 5 5. The set point was reduced to 110°C (230°F) and allowed to stir overnight.
6. In the morning, the batch was cooled to 90°C (194°F) and the batch was sampled. Gas chromatographic (GC) analysis showed the material to be 96.1% desired product and to contain no amide. Charge E was added.
- 10 10. The batch was stirred for 30 minutes, allowed to phase split and the upper water phase was vacuum decanted off. The operation was repeated for Charge F at 63°C (145°F).
- 15 7. After the water washes, the batch was agitated with Charge G for 30 minutes at 63°C (145°F), then was phase split, and vacuum decanted. The pH of the water layer was tested and found to be less than 2.
8. After the acid wash, the batch was washed with water charges H, I, and J successively at 63°C (145°F).
- 20 9. The batch was melted and poured out of the flask into a bottle and allowed to solidify. A small amount of water on top of the resulting solid was poured off, and the remaining solid material in the jar was found to weigh 124 g.
- 25 10. The solid material was melted into a two-necked 500 ml flask. The melting point was found to be 57°C (135°F).
11. The resulting liquid material (113 g) was distilled at 667 - 933 Pa (5-7 torr Hg). 104 g (92% of undistilled material) distilled at a head temperature of 130-137°C (266-279°F) and a pot temperature of 136-152°C (277-306°F). Further increase of the pot temperature to 170°C (338°F) resulted in no further material distilling over.
- 30

**Preparation of MeFBSEA (N-methyl-perfluorobutane
sulfonylethyl acrylate)**

REACTION:



CHARGES:

- A. 112 g MeFBSE alcohol ($\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$, 0.313 moles)
10 B. 0.07 g phenothiazine (available from Sigma-Aldrich,
 Milwaukee, WI)
 C. 0.11 g methoxyhydroquinone (MEHQ) (available from
 Sigma-Aldrich, Milwaukee, WI)
 D. 100 g heptane
15 E. 27.5 g acrylic acid (0.38 moles)
 F. 1 g anhydrous triflic (trifluoromethanesulfonic) acid
 (available as FC-24 from 3M, Maplewood, MN)
 G. 300 g water
 H. 300 g water

20

PROCEDURE:

1. Charges A, B, C, D, E and F were added to a 3-necked
 flask equipped with decanter assembly, overhead
 stirrer, and a thermocouple under positive nitrogen
25 pressure.
2. The flask was warmed to 60°C and the stirring was
 begun. The batch was stirred at reflux which was
 initially at 96°C and rose to 102°C by the end of the
 reaction. The theoretical water that should be
30 collected in the decanter was 6.3 ml. After 15 minutes
 of refluxing, 2 ml had collected. After 1 hour and 15
 minutes, the reflux temperature was 99°C and 5 ml had
 collected. After 5 hours and 15 minutes the reflux

temperature was 102°C and 5.4 ml had collected. A sample was withdrawn from the batch and GC analysis showed no unreacted alcohol, 92.6% desired product and 7.4% high boiler that is probably the Michael adduct with acrylic acid.

3. The batch was stripped atmospherically to the decanter until at 103°C no more heptane collected in it.
4. The batch was cooled to 64°C and vacuum was pulled slowly. More heptane was stripped off until at 5 torr no more liquid was observed to be distilling off.
5. Vacuum was broken and Charge G was added. The batch was stirred at 64°C for 15 minutes, allowed to phase spilt and the upper layer was vacuumed off.
6. This operation was repeated with Charge H and then the batch was allowed to cool to room temperature at which point the product was a solid. The remaining water was poured off and the product material was melted out of the container into a jar. The weight of the product was 125 g (theoretical 129 g). GC analysis showed the material to be 92.64% desired acrylate and 7.36% acrylic acid Michael adduct.

Preparation 2: Synthesis of MeFBSEMA

MeFBSEMA can be prepared as described in Preparation 1 above, except using methacrylic acid in place of acrylic acid.

FC-1: Preparation of MeFBSEA (30%)/CW750A (65%)/AMPS (5%)

A random acrylic copolymer of MeFBSEA (30 weight %) with CW750A (65 weight %) and AMPS monomer was prepared. The following charges were added to a 500 ml flask under positive nitrogen pressure:

CHARGES:

15 g MeFBSEA
32.5 g CW750A
2.5 g AMPS
5 2.5 g 2,2'-Azobisisobutyronitrile (available as VAZO™
from Sigma-Aldrich, Milwaukee, WI)
2.0 g 3-mercapto-1,2-propanediol (available from
Sigma-Aldrich, Milwaukee, WI)
117 g N-(methyl)pyrrolidinone (available from Sigma-
10 Aldrich, Milwaukee, WI)
2.8 g N-Methyldiethanolamine (available from Sigma-
Aldrich, Milwaukee, WI)

The batch was heated to 79°C for 5 hours. The solids content
was found to be 27.1 % by weight of the resulting polymer
15 solution by evaporation of a small quantity. Analysis of
the polymer solution for residual monomer was done using a
flame ionization GC, using N,N-Diethyl-m-Toluamide
(available from Sigma-Aldrich, Milwaukee, WI) as an internal
standard in N,N-Dimethylacetamide (available from Sigma-
20 Aldrich, Milwaukee, WI), and obtaining calibration curves
with the MeFBSEA and the internal standard. Weight %
residual MeFBSEA was found to be 0.0201%.

FC-2: Preparation of MeFBSEA (38%)/Pluronic Acrylate (62%)

25 A random copolymer surfactant of MEFBSEA (38
weight %) with Pluronic acrylate (62 weight %) was prepared.

CHARGES:

570 g Me-FBSEA
1431 g Pluronic acrylate 65% in Toluene
30 685 g toluene
73 g 3-mercapto-1,2-propanediol
29 g N-(methyl)pyrrolidinone

73 g 50% t-butyl peroctoate (available as Luperox™
26M50 from Atofina Chemicals, Inc., Philadelphia, PA)

Charges A through E were charged to a five liter flask
5 equipped with an overhead stirrer, thermocouple, reflux
condenser with nitrogen flow though the opening used for
charging. After charging, the batch was kept under slight
positive nitrogen pressure to exclude oxygen from the batch.
The temperature set point was raised to 80°C. Charge F was
10 added. Due to the initial exotherm, the batch heated itself
to 90°C. A temperature control timer was set for 5 hours
and the batch was left for the night. The next day, the
reflux condenser was replaced with a one-plate distillation
apparatus. Toluene was stripped off at 10-20 mm pressure
15 until the pot temperature rose to 75°C. The resulting
contents were poured out and weighed. A total of 1575 g of
thick amber liquid was isolated and poured into jars at
50°C.

20 **FC-3: Preparation of MeFBSEMA (55%)/CW750A (35%)/Acrylic
Acid (10%)**

A random copolymer surfactant of MeFBSEMA (55
weight %) with CW750A (35 weight %) and acrylic acid (10
weight %) was prepared. The following charges were added to
25 a 1000 ml flask under positive nitrogen pressure:

55 g MeFBSEMA
35 g CW750A
10 g acrylic acid
6 g t-butyl peroctoate (50% solids in mineral spirits)
30 1 g 3-mercapto-1,2-propanediol
100 g ethyl acetate

The batch was heated to 79°C for 8 hours. The solids content was found to be 48.1% by weight of the resulting polymer solution by evaporation of a small quantity.

5 **FC-4: Preparation of MeFBSEA (35%)/CW750A (61%)/Acrylic Acid (2%)/DMAEMA (2%)**

 A random copolymer surfactant of MeFBSEA (35 weight %) with CW750A (61 weight %), acrylic acid (2 weight %), and DMAEMA (2 weight %) was prepared. The following
10 charges were added to a 1000 ml flask under positive nitrogen pressure:

 35 g MeFBSEA
 61 g CW750A
 2 g acrylic acid
15 2 g DMAEMA
 8 g t-butyl peroctoate (50% solids in mineral spirits)
 3 g 3-mercapto-1,2-propanediol
 100 g ethyl acetate

 The batch was heated to 79°C for 8 hours. The solids content
20 was found to be 48.1% by weight of the resulting polymer solution by evaporation of a small quantity.

FC-5: Preparation of MeFBSEMA (35%)/CW750A (63%)/AA (2%)

 A random copolymer surfactant of MeFBSEMA (35 weight %) with CW750A (63 weight %), and acrylic acid (2 weight %) was prepared. The following charges were added to
25 a 1000 ml flask under positive nitrogen pressure:

 35 g MeFBSEMA
 63 g CW750A
30 2 g acrylic acid
 6 g t-butyl peroctoate (50% solids in mineral spirits)
 1 g 3-mercapto-1,2-propanediol

100 g ethyl acetate

The batch was heated to 79°C for 8 hours. The solids content was found to be 48.1% by weight of the resulting polymer solution by evaporation of a small quantity.

5

FC-6: Preparation of $C_4F_9SO_2N(CH_3)(CH_2CH_2O)_{7.5}CH_3$

FC-6 was prepared as described in WO 01/30873, Example 1.

10

FC-7: Preparation of MeFBSEA (55%)/Pluronic Acrylate (45%)

FC-7 was prepared using the procedure described above for the preparation of FC-2 with the exception that the weight ratio of MeFBSEA/Pluronic acrylate was adjusted to 55/45.

15

FC-8: Preparation of Bu-FOSEA (30%)/Pluronic Acrylate (70%)

FC-8 was prepared as described in U.S. Patent No. 3,787,351 (Olson), Example 1.

20

FC-9: Preparation of $C_8F_{17}SO_2N(Et)(CH_2CH_2O)_{13}H$

FC-9 was prepared as described in U.S. Patent No. 2,915,554 (Ahlbrecht et al.), Example 2 where $n = 13$).

25

FC-10: Preparation of MeFBSEMA (53%)/Stearyl Methacrylate (33%)/AA (14%)

A random copolymer surfactant of MeFBSEMA (53 weight %) with stearyl methacrylate (33 weight %) and acrylic acid (14 weight %) was prepared. The following charges were added to a 1000 ml flask under positive nitrogen pressure:

30

53 g MeFBSEMA
33 g stearyl methacrylate
14 g acrylic acid

6 g t-butyl peroctoate (50% solids in mineral spirits)

3 g mercaptopropanediol 100 g ethyl acetate

The batch was heated to 79°C for 6 hours. The solids content was found to be 46.7% by weight of the resulting polymer solution by evaporation of a small quantity.

FC-11: Preparation of MeFBSEA (38%)/Pluronic Acrylate (60%) /AA (2%)

FC-11 was prepared using the procedure described above for the preparation of FC-2 with the exception that the weight ratio of MeFBSEA/Pluronic acrylate was adjusted to 38/60 and 2% AA was added.

FC-12: Preparation of MeFBSEA (30%)/Stearyl methacrylate (30%)/CW750A (30%)/AMPS (10%)

FC-12 was prepared using the procedure described above for the preparation of FC-1 with the exception that the weight ratio of MeFBSEA/CW750A was adjusted to 30/30, stearyl methacrylate/AMPS was added at the weight ratio of 30/10.

FC-13: Preparation of MeFBSEMA (30%)/CW750A (70%)

FC-13 was prepared using the procedure described above for the preparation of FC-5 with the exception that the weight ratio of MeFBSEMA/CW750A was adjusted to 30/70 and no AA was added.

FC-14: Preparation of MeFBSEA (40%)/CW750A (51%)/AMPS (5%)/DMAEMA (4%)

FC-14 was prepared using the procedure described above for the preparation of FC-1 with the exception that the weight ratio of MeFBSEA/CW750A/AMPS was adjusted to 40/51/5 and DMAEMA was added at 4%.

FC-15: Preparation of MeFBSEA (50%)/CW750A (50%)

FC-15 was prepared using the procedure described above for the preparation of FC-3 with the exception that
5 MeFBSEMA was replaced with MeFBSEA, no AA was added and the weight ratio of MeFBSEA to CW750A was 50/50

Preparation of Latex Paint Compositions**Examples 1 - 16**

10 A 1 L jacketed stainless steel beaker was charged with the grind: Joncryl (161.50 g), Propylene glycol (31.45 g), Drew (2.55 g) Ti-Pure (170.00 g) Supermite (134.51 g) Novacite (75.23 g) and Attagel (8.50 g). Cooling water was
15 then turned on and the resulting mixture was dispersed at high speed (11,000 rpm) using a high shear Cowles mixer, equipped with a 32 mm Cowles impeller for about 30 minutes. The high shear Cowles mixer was then replaced with a low shear marine impeller mixer running at 200 rpm and the mixture was let down by adding the letdown: Joncryl (136.00
20 g), Deionized (DI) Water (223.43 g), Drew (0.85 g) Acrysol (15.30 g), Texanol (18.21 g), Butyl Carbitol (9.37g), fluorochemical additive (8.35 g premixed 10% active weight per weight in Texanol), Colortrend (4.56 g) and Nuosept
(1.28 g).

25

Comparative Examples C1 - C5

Table 1 and Table 2 list the compositions of the grind and the letdown for Comparative Examples C1 through C5. Comparative Examples C1 through C5 were prepared
30 following the general procedure used for the preparation of the paint compositions for Examples 1 through 16 above, but with appropriate amounts of materials as cited in the Tables

1 and 2.

Table 1

Comparative Examples C1 - C5 Grind Ingredients (in grams)

5

Ex	Joncryn	DI Water	Propylene Glycol	Drew	Ti- Pure	Supermite	Kaolin	Novacite	Attagel
C1	161.50	---	31.45	2.55	170.00	134.51	----	75.23	8.50
C2	297.50	79.73	31.45	2.55	170.00	----	263.53	75.23	----
C3	297.50	79.73	31.45	2.55	170.00	----	263.53	75.23	----
C4	234.17	----	31.45	2.55	170.00	267.12	----	75.23	8.50
C5	268.54	----	31.45	2.55	170.00	----	143.57	75.23	----

Table 2

Comparative Examples C1 - C5 Letdown Ingredients (in grams)

10

Ex	Joncryn	DI Water	Drew	Texanol	Butyl Carbitol	Color Trend	Nuosept	NH ₄ OH	Acrysol	FC
C1	136.00	223.43	0.85	15.48	9.37	4.56	1.28	1.50	15.30	----
C2	----	98.11	0.85	2.75	9.37	4.56	1.28	1.28	8.50	FC-2 21.24
C3	----	98.11	0.85	23.99	9.37	4.56	1.28	1.28	8.50	----
C4	63.33	177.20	0.85	23.99	9.37	4.56	1.28	1.28	11.90	----
C5	28.96	223.93	0.85	23.99	9.37	4.56	1.28	1.28	10.20	----

Comparative Examples C6 - C11

15 Comparative Examples C6 through C11 were prepared following the general procedure used for the preparation of the paint compositions for Examples 1 through 16 above, but with the appropriate fluorochemical additive as cited in the Table 3.

Table 3

Comparative Examples C6 - C11 Fluorochemical Additives

Ex	FC
C6	Zonyl
C7	FC-10
C8	FC-7
C9	FC-8
C10	FC-6
C11	FC-9

Coating Method and Testing**5 Coating Method for Stain Release Testing**

The latex paint samples were prepared by coating onto a black scrub test panel (Form P121-10N; 16.5 cm x 43.2 cm; available from The Leneta Co., Mahwah, NJ) using a hand coater with a 6 mil (0.15 mm) gap. The resulting latex
10 paint coating was allowed to air dry at ambient temperature and humidity for 7 days.

Soiling/Cleaning Test Method

"Greasy dirt" was prepared by high shear mixing of
15 50 parts Lanolin (USP anhydrous), 50 parts Petrolatum, 5 parts carbon black, 30 parts stick margarine, and 10 parts mineral oil at 120°F (50°C) for about 15 minutes. The resulting greasy dirt was applied onto the coated test panel with a 3" (7.62 cm) paint roller and allowed to set for 18 -
20 24 hours. The resulting dirty panel was vigorously rubbed with a clean paper towel to remove as much of the greasy dirt as possible. The panel (painted side up) was then affixed to a Gardner Scrub Machine (available from Gardner Laboratories, Bethesda, Maryland). A cellulosic sponge,
25 saturated with 5% DAWN™ dishwashing liquid in DI water

(available from Procter & Gamble, Cincinnati, OH) and squeezed to remove the bulk of the dishwashing solution, was placed into the scrub machine brush holder. About 200 ml DAWN™ dishwashing liquid (5% in DI water) was applied to the painted and dirtied surface of the scrub test panel. The scrubbing was stopped after 17 double scrubs and the test panel was removed, rinsed with DI water, and air-dried for at least one hour.

10 Residual Stain Measurement

Residual stain measurements were taken using a Minolta CR200 Chroma meter (available from Minolta Corp, Osaka, Japan) with D65 illuminant. L*, a*, and b* measurements of the unstained portion of the scrub test panel (designated with subscript "u" in the formula below) and stained portion of the scrub test panel (designated with the subscript "s" in the formula below) were taken. To calculate the residual stain, ΔE, the following formula was used:

$$\Delta E = \sqrt{(L^*_u - L^*_s)^2 + (a^*_u - a^*_s)^2 + (b^*_u - b^*_s)^2}$$

This ΔE value represents the distance in the L*a*b* color space between the unstained area and the stained area (see, for example, Richard S. Hunter, THE MEASUREMENT OF APPEARANCE, Wiley-Interscience, pp. 102-130, (1975)). It is a good measurement for the difference in color as perceived by people. The smaller the ΔE value, the cleaner the surface.

30 Static Contact Angle Test Method

The paint to be tested was coated onto a standard Leneta Scrub test panel using a 6 mil (0.15 mm) gap coater. After drying at ambient conditions for 3 days, a 0.5" (1 cm) by 2" (5 cm) strip was cut from the coated area. The resulting strip was placed on a goniometer (NRI C. A. Goniometer, Model 100-00-US made by Rame-Hart Inc, Mountain Lake, NJ) viewing stage. A minimum volume drop of reagent grade hexadecane was allowed to fall (from a 5 ml micrometer syringe, equipped with an 18 gage hypodermic needle) onto the coated strip from about ¼" (6 mm). The goniometer viewing light was turned on and the drop was brought into focus. The viewing stage was adjusted to align the zero degree reference line with the bottom of the drop. The movable protractor line was rotated until it was superimposed with the contact angle of the drop. The contact angle was read from the scale. In this test, an angle of 0 degrees means complete wetting, and increasing angles mean a more oil repellent (surface energies less than hexadecane surface energy) surface.

Table 4 lists the results of the Residual Stain Measurement Tests (ΔE) and static contact angle values ($^{\circ}$).

Table 4

Example	Description	ΔE	Static Contact Angle ($^{\circ}$)
C1	no Fluorochemical additive	13.35*	0
C2	High PVC, Clay w/ FC-2	8.80	42
C3	60% PVC, clay, no Fluorochemical additive	18.93	0
C4	60% PVC, CaCO ₃ , no Fluorochemical additive	18.11	0
C5	52% PVC, clay, no Fluorochemical additive	15.34	0

C6	Zonyl	0.58	60
C7	FC-10	9.22	27
C8	FC-7	11.92	16
C9	FC-8	11.95	65
C10	FC-6	13.58	68
C11	FC-9	15.02	
1	FC-2/FC-3 (75/25)	0.37	
2	FC-11	0.4	59
3	FC-3	0.4	
4	FC-5	0.4	
5	FC-3	0.44	56
6	FC-12	0.45	55
7	FC-4	0.54	43
8	FC-13	0.6	46
9	FC-1	0.66	57
10	FC-14	0.70	62
11	FC-15	0.89	56
12	FC-2	1.01	

*Average of two runs

Results listed in Table 4 indicate that latex paints of the invention (Examples 1 - 12) perform better than latex paints containing no fluorochemical additive. Additionally, latex paint compositions prepared using perfluorooctanesulfonate derivatives (Comparative Examples C9 & C11) did not exhibit as good ΔE values as those prepared using perfluorobutanesulfonate derivatives of the invention. (Examples 1 - 12).

Drying Condition Tests

Examples 13 - 15

A paint composition containing FC-2 such as that prepared for Example 12 was used to coat three samples panels as described above. The coated sample panel for Example 15 was dried in a circulating air oven for 3 days. The coated sample panel for Example 16 was dried under ambient conditions (about 22°C (72°F) and less than approximately 55% humidity) for 3 days. The coated sample

panel for Example 17 was dried at a controlled temperature of 21°C (70°F) and relative humidity of 70% for 3 days. The Soiling/Cleaning Test was performed on the resulting samples and residual stain measurements were taken. The resulting
5 ΔE values are listed in Table 5.

Examples 16 - 19

Fluorochemical additive was prepared as described in the preparation of FC-2 above, with the exception that the reaction temperature set point for Examples 16 and 18
10 was set to 90°C instead of 80°C and for Examples 17 and 19 the reaction set point was set to 70°C instead of 80°C. A paint composition such as that prepared for Example 12, with the exception that 0.1 weight per volume percent
15 fluorochemical additive was added instead of 0.3 weight per volume percent, was used in coating the resulting samples, substituting the appropriate temperature-modified
fluorochemical additive as described. Each coated sample panel was dried at a given temperature and relative humidity
20 for 3 days. The Soiling/Cleaning Test was performed on the resulting samples and residual stain measurements were taken. The resulting ΔE values are listed in Table 5.

Table 5

Example	Temperature °C (°F)	% Relative Humidity	ΔE
13	52 (125)	< 10	4.29
14	Approx. 22 (72)	< Approx. 55	0.50
15	21 (70)	70	0.16
16	22 (72)	55	0.59
17	22 (72)	55	0.24
18	21 (70)	70	0.29

19	21 (70)	70	0.25
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The results listed in Table 5 indicate that latex paint compositions of the invention dried at very low relative humidity and high temperature (Example 13) exhibit poorer cleanability (that is, higher ΔE values) than samples dried at lower temperatures and higher relative humidity (Examples 14 - 19).

Electron Spectroscopy for Chemical Analysis (ESCA)

ESCA Test Method

ESCA measurements were performed on a Surface Science SSX-100 instrument (formerly available from Surface Science, Mountain View, CA). This equipment excites photoelectrons using a non-monochromated Al x-ray source. Emitted photoelectrons were detected at a 35° take-off angle with respect to the sample surface. Spectra were obtained and the surface composition was determined by integrating the major peak areas and applying the appropriate sensitivity factors. A typical fluorine detection level is 1-2 atom percent. To determine sub-surface fluorine concentration the sample was sliced using a Ultra Cut-T with FCS cryo microtome (available from Mager Scientific, Dexter, MI). Each cut with the cryo-microtome removed 1 μm of painted surface.

Example 20

Paint prepared as in Example 12 was applied to glass microscope slides and dried at ambient temperature and relative humidity. The cut # indicates the number of the consecutive 1- μm cuts taken from the "as painted" original surface. The as painted original surface and cuts 9, 16,

20, and 25 were tested for fluorine levels using the ESCA test method. Results are listed in Table 6.

Table 6

5

Cut #	Fluorine (atom percent)
As painted original surface	18
9	Not detectable
16	Not detectable
20	Not detectable
25	Not detectable

The data in Table 6 indicate that the majority of fluorochemical additive has migrated to the surface of the dried paint coating.

10

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention.

15

What is claimed:

1. A latex paint composition comprising (a) a
5 polymer having interpolymerized units that comprise units
derived from styrene, methyl styrene, vinyl, or combinations
thereof and units derived from one or more acrylates,
methacrylates, acrylonitrile, or combinations thereof, (b)
hiding pigment, (c) non-cellulosic thickener, and (d) at
10 least about 0.05 weight per volume percent fluorochemical
acrylic polymer additive comprising (1) at least one
perfluoroalkyl moiety selected from the group consisting of
heptafluoropropanesulfonamido, nonafluorobutanesulfonamido,
undecafluoropentanesulfonamido, and
15 tridecafluorohexanesulfonamido moieties and (2) at least one
polyoxyalkylene block comprising at least one alkyleneoxy
moiety; wherein said fluorochemical acrylic polymer additive
comprises about 5 to about 30 weight percent carbon-bonded
fluorine based upon the total weight of said fluorochemical
20 acrylic polymer, and said latex paint composition has a
pigment volume concentration of at least 20% and less than
its critical pigment volume concentration.

2. The paint composition of claim 1 wherein said
25 perfluoroalkyl moiety is nonafluorobutanesulfonamido.

3. The paint composition of claim 1 wherein a
plurality of said perfluoroalkyl moieties are each linked to
at least one said polyoxyalkylene block by a polymeric
30 chain.

4. The paint composition of claim 1 wherein said
alkyleneoxy moiety is selected from the group consisting of

ethyleneoxy moieties and propyleneoxy moieties.

5 5. The paint composition of claim 4 wherein a polyoxypropylene block having at least one said propyleneoxy moiety is attached to a polyoxyethylene block having at least one ethyleneoxy moiety.

10 6. The paint composition of claim 5 wherein said polyoxypropylene block is also attached to a second polyoxyethylene block.

15 7. The paint composition of claim 6 wherein both said polyoxyethylene blocks have from about 5 to about 130 ethyleneoxy moieties and said polyoxypropylene block has from about 20 to about 55 propyleneoxy moieties.

20 8. The paint composition of claim 5 wherein said polyoxyethylene block is also attached to a second polyoxypropylene block.

25 9. The paint composition of claim 7 wherein both said polyoxypropylene blocks have from about 5 to about 25 propyleneoxy moieties and said polyoxyethylene block has from about 10 to about 165 ethyleneoxy moieties.

30 10. The paint composition of claim 1 wherein said fluorochemical acrylic polymer additive has about 10 to about 25 weight percent carbon-bonded fluorine based upon the total weight of said fluorochemical acrylic polymer.

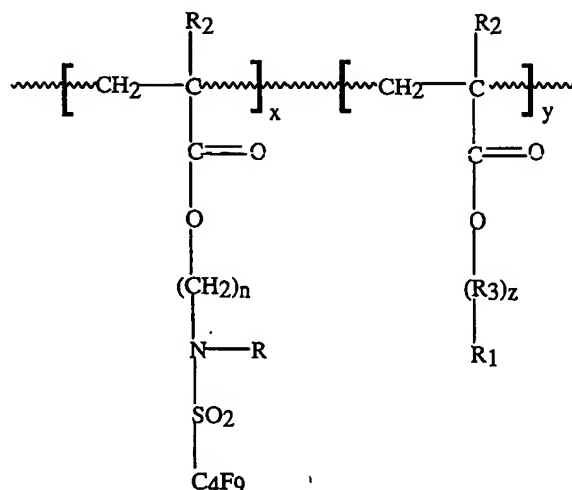
 11. The paint composition of claim 1 wherein said alkyleneoxy moiety is derived from a polyethylene glycol having an average molecular weight of about 200 to about

10,000.

12. The paint composition of claim 1 wherein said fluorochemical acrylic polymer additive further comprises an anionic water-solubilizing polar group.

13. The paint composition of claim 12 wherein said anionic water-solubilizing polar group is selected from the group consisting of sulfonates, sulfates, and carboxylates.

14. The paint composition of claim 1 wherein said fluorochemical acrylic polymer additive is selected from those represented by the following general formula:



wherein:

~~~~~ represents a bond in a polymerizable or polymer chain;

R, R<sub>1</sub> and R<sub>2</sub> are each independently hydrogen or alkyl of 1 to 4 carbon atoms;

R<sub>3</sub> is at least one or more straight or branched alkyleneoxy groups, linked together and having 2 to 6

carbon atoms, or a straight or branched alkylene group having 12 to 20 carbon atoms;

n is an integer from 2 to 10; and

x, y and z are integers of at least 1.

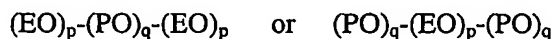
5

15. The paint composition of claim 14 wherein said R, R<sub>1</sub>, and R<sub>2</sub> are each independently hydrogen or methyl.

16. The paint composition of claim 14 wherein  
10 said n is 2.

17. The paint composition of claim 14 wherein said R<sub>3</sub> is a group selected from those represented by the following general formulas:

15



wherein:

EO is an ethyleneoxy moiety;

PO is a propyleneoxy moiety;

20 p is an integer of 1 to about 165; and

q is an integer of 0 to about 55.

18. The paint composition of claim 17 wherein said R<sub>3</sub> is represented by the following general formula:

25



19. The paint composition of claim 18 wherein said q is an integer of about 5 to about 25 and said p is an integer from about 10 to about 165.

30

20. The paint composition of claim 17 wherein said R<sub>3</sub> is represented by the following general formula:



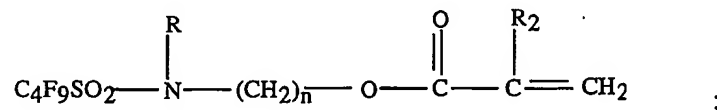
21. The paint composition of claim 20 wherein  
said p is an integer of about 5 to about 130 and said q is  
5 an integer of about 20 to about 55.

22. The paint composition of claim 21 wherein  
said p is about 11 and said q is about 21.

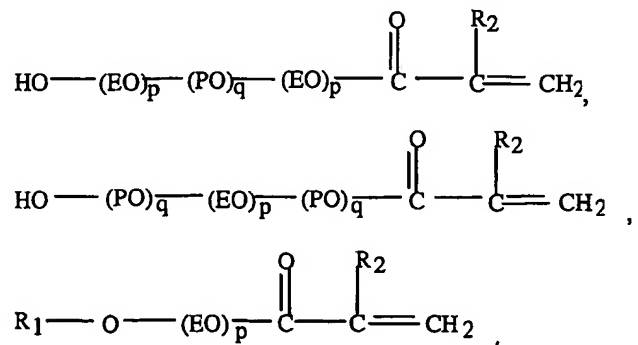
10 23. The paint composition of claim 22 wherein  
said R is methyl.

24. The paint composition of claim 1 wherein said  
fluorochemical acrylic polymer additive comprises the  
15 reaction product of:

(i) a compound represented by the following  
general formula:

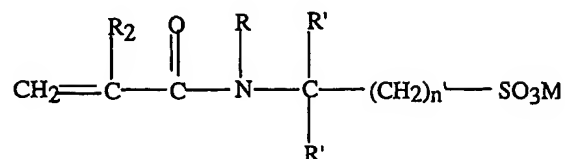


20 (ii) a compound selected from the group consisting  
of



25 and mixtures thereof; and

(iii) a compound represented by the following general formula:



wherein:

5           R, R<sub>1</sub>, R<sub>2</sub>, R' are hydrogen or alkyl of 1 to 4 carbon atoms,

n is an integer of 2 to about 10,

EO is an ethyleneoxy moiety,

PO is a propyleneoxy moiety,

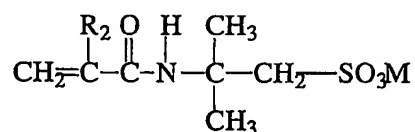
10           p is an integer of 1 to about 130,

q is an integer of 0 to about 55,

n' is an integer of 1 to about 10, and

M is hydrogen or a cation.

15           25. The paint composition of claim 24 wherein (iii) is a compound represented by the following general formula:



wherein:

20           R<sub>2</sub> is hydrogen or methyl and M is hydrogen, potassium, ammonium, lithium, or a protonated tertiary amine.

25           26. The paint composition of claim 24 wherein said fluorochemical acrylic polymer additive comprises the reaction product of (i), (ii), (iii), and (iv); wherein (iv) is a compound represented by the following general formula:



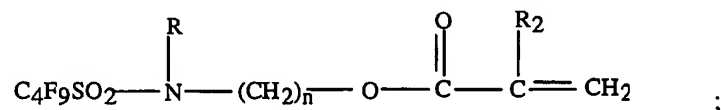
wherein:

A is an amine-containing group or an alkyl of 12 to 20 carbon atoms.

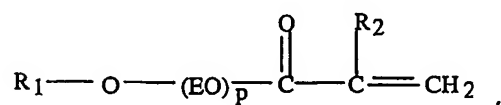
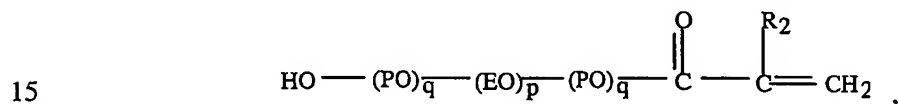
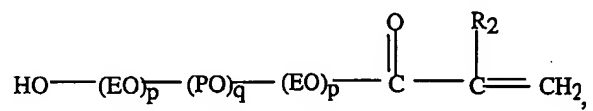
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27. The paint composition of claim 1 wherein said fluorochemical acrylic polymer additive comprises the reaction product of:

10 (i) a compound represented by the following general formula:

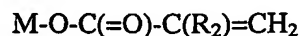


(ii) a compound selected from the group consisting of



and mixtures thereof; and

20 (iii) a compound represented by the following general formula:



wherein:

R, R<sub>1</sub>, R<sub>2</sub>, and R' are independently hydrogen or alkyl of 1 to 4 carbons atoms,

25 n is an integer of 2 to about 10,

EO is an ethyleneoxy moiety,

PO is a propyleneoxy moiety,



p is an integer of 1 to about 130,  
q is an integer of 0 to about 55, and  
M is H, potassium, sodium, ammonium, or protonated  
tertiary amine.

5

28. The paint composition of claim 27 wherein  
said M is H or ammonium.

29. The paint composition of claim 27 wherein  
10 said fluorochemical acrylic polymer additive comprises the  
reaction product of (i), (ii), (iii), and (iv); wherein (iv)  
is a compound represented by the following general formula:



15        wherein:

A is an amine-containing group or an alkyl of 12  
to 20 carbon atoms.

30. The paint composition of claim 1 wherein said  
20 interpolymerized units comprise at least 40 mole percent of  
units derived from styrene, methyl styrene, or combinations  
thereof and at least 10 mole percent of units derived from  
one or more acrylates, methacrylates, acrylonitrile, or  
combinations thereof.

25

31. The paint composition of claim 30 wherein  
said interpolymerized units comprise units derived from 2-  
ethylhexyl acrylate.

30        32. The paint composition of claim 30 wherein  
said interpolymerized units comprise from 50 to 70 mole  
percent of units derived from styrene, methyl styrene, or  
combinations thereof; from 10 to 30 mole percent of units

derived from 2-ethylhexyl acrylate; and from 10 to 30 mole percent of units derived from methyl acrylate, acrylonitrile, or combinations thereof.

5                   33. The paint composition of claim 30 wherein said interpolymerized units consist essentially of units derived from two or more monomers selected from the group consisting of styrene, methyl styrene, acrylates, methacrylates, and acrylonitrile.

10

                  34. The paint composition of claim 30 wherein said acrylates and methacrylates contain from about 4 to about 16 carbon atoms.

15                   35. The paint composition of claim 1 wherein said polymer has a glass-transition temperature between 21°C and 95°C.

20                   36. The paint composition of claim 1 wherein said hiding pigment has an index of refraction above about 1.8.

                  37. The paint composition of claim 1 wherein thickener is an associative thickener.

25                   38. The paint composition of claim 37 wherein said thickener is a polyurethane associative thickener.

                  39. The paint composition of claim 1 wherein said latex paint further comprises a flatting agent and has an  
30   85° gloss of less than or equal to about 20.

40. The paint composition of claim 39 wherein said flatting agent is silica.

5 41. The paint composition of claim 1 wherein said latex paint has a pigment volume concentration of less than about 55%.

42. The paint composition of claim 1 wherein said latex paint further comprises a calcium carbonate functional  
10 extender.

43. The paint composition of claim 1 wherein said latex paint further comprises a coalescing solvent.

15 44. The paint composition of claim 43 wherein said coalescing solvent is butyldiglycol, 2,2,4-trimethyl-1,3-pentandiol-monoisobutyrate, or combinations thereof.

20 45. An article wherein a portion of at least one surface of said article is coated with the paint composition of claim 1.

46. A method of imparting stain and soil resistance to a latex paint coating comprising the steps of  
25 (a) providing a latex paint composition comprising (1) a polymer having interpolymerized units that comprise units derived from styrene, methyl styrene, vinyl, or combinations thereof and units derived from one or more acrylates, methacrylates, acrylonitrile, or combinations thereof, (2)  
30 hiding pigment, and (3) non-cellulosic thickener; wherein said latex paint has a pigment volume concentration of at least 20% and less than its critical pigment volume concentration;

(b) adding at least about 0.05 weight per volume percent of a fluorochemical acrylic polymer additive comprising (1) at least one perfluoroalkyl moiety selected from the group consisting of heptafluoropropanesulfonamido, nonafluorobutanesulfonamido, undecafluoropentanesulfonamido, and tridecafluorohexanesulfonamido moieties and (2) at least one polyoxyalkylene block comprising at least one alkyleneoxy moiety; wherein said fluorochemical acrylic polymer has about 5 to about 30 weight percent carbon-bonded fluorine based upon the total weight of said fluorochemical acrylic polymer to said latex paint composition;

(c) applying the resulting composition of (b) to a substrate surface; and

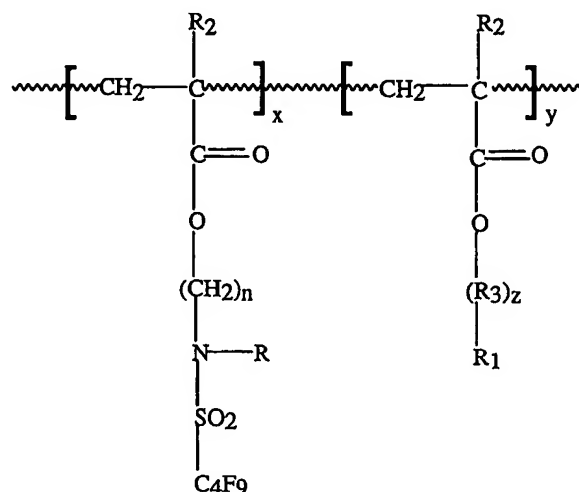
(d) allowing said resulting composition to dry such that a coating with a fluorine-enriched surface is formed on said substrate surface.

47. The method of claim 46 wherein said interpolymerized units comprise at least 40 mole percent of units derived from styrene, methyl styrene, or combinations thereof and at least 10 mole percent of units derived from one or more acrylates, methacrylates, acrylonitrile, or combinations thereof.

48. The method of claim 46 wherein said polymer has a glass-transition temperature between 21°C and 95°C.

49. The method of claim 46 wherein said resulting composition is allowed to dry at a temperature of about 10°C to about 40°C and a relative humidity of about 20% to about 90%.

50. The method of claim 46 wherein said fluorochemical acrylic polymer additive is selected from those represented by the following general formula:



5 wherein:

~~~~~ represents a bond in a polymerizable or polymer chain;

R, R₁ and R₂ are each independently hydrogen or alkyl of 1 to 4 carbon atoms;

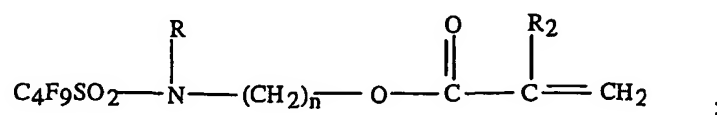
10 R₃ is at least one or more straight or branched alkylene-oxy groups, linked together and having 2 to 6 carbon atoms, or a straight or branched alkylene group having 12 to 20 carbon atoms;

n is an integer from 2 to 10; and

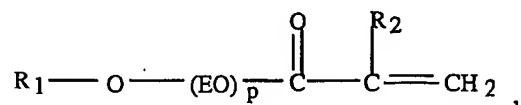
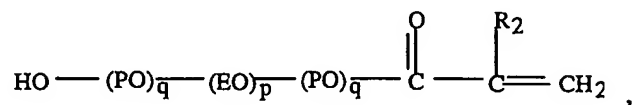
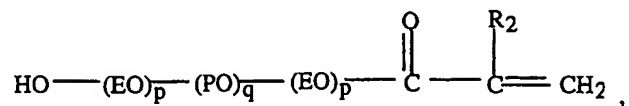
15 x, y and z are integers of at least 1.

51. The method of claim 46 wherein said fluorochemical acrylic polymer additive comprises the reaction product of:

20 (i) a compound represented by the following general formula:

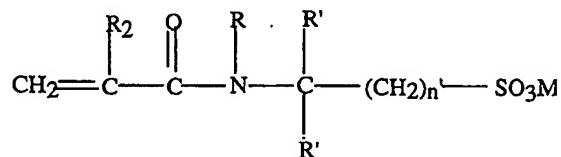


(ii) a compound selected from the group consisting of



and mixtures thereof; and

(iii) a compound represented by the following general formula:



wherein:

R, R₁, R₂, R' are hydrogen or alkyl of 1 to 4 carbon atoms,

n is an integer of 2 to about 10,

EO is an ethyleneoxy moiety,

PO is a propyleneoxy moiety,

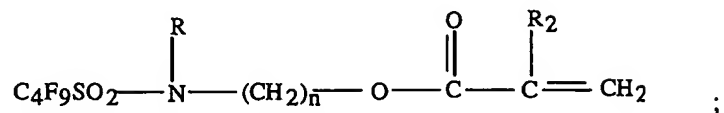
p is an integer of 1 to about 128,

q is an integer of 0 to about 55, and

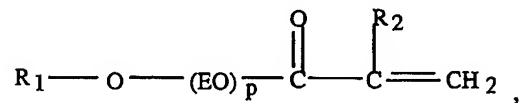
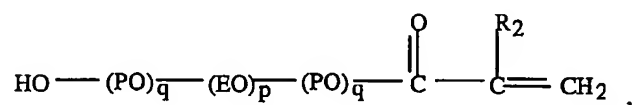
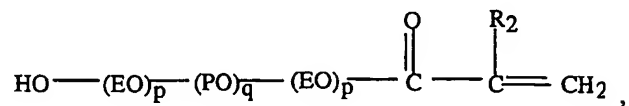
n' is an integer of 1 to about 10.

52. The method of claim 46 wherein said fluorochemical acrylic polymer additive comprises the reaction product of:

(i) a compound represented by the following general formula:



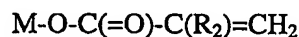
5 of (ii) a compound selected from the group consisting



and mixtures thereof; and

10

(iii) a compound represented by the following general formula:



wherein:

15

R, R₁, R₂, and R' are independently hydrogen or alkyl of 1 to 4 carbons atoms,

n is an integer of 2 to about 10,

EO is an ethyleneoxy moiety,

PO is a propyleneoxy moiety,

20

p is an integer of 1 to about 130,

q is an integer of 0 to about 55, and

M is H, potassium, sodium, ammonium, or protonated tertiary amine.

25

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/14831A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D125/12 C09D125/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| A | EP 0 614 955 A (MINNESOTA MINING)
14 September 1994 (1994-09-14)
cited in the application
whole document | 1-52 |
| P,A | US 6 492 477 B1 (3M INNOVATIVE PROPERTIES)
10 December 2002 (2002-12-10)
whole document | 1-52 |

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

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- *G* document member of the same patent family

Date of the actual completion of the international search

2 September 2003

Date of mailing of the international search report

09/09/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Trauner, H-G

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/14831

| Patent document
cited in search report | Publication
date | Patent family
member(s) | Publication
date |
|---|---------------------|----------------------------|---------------------------|
| EP 0614955 | A | 14-09-1994 | AU 666797 B2 22-02-1996 |
| | | | AU 5493794 A 15-09-1994 |
| | | | CA 2114706 A1 09-09-1994 |
| | | | DE 69410004 D1 10-06-1998 |
| | | | DE 69410004 T2 03-09-1998 |
| | | | EP 0614955 A1 14-09-1994 |
| | | | ZA 9400791 A 04-08-1995 |
| US 6492477 | B1 | NONE | |